A Comprehensive Environmental Assessment Approach to Making Informed Decisions about Engineered Nanoparticles

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **MAY 2011**	2. REPORT TYPE	3. DATES COVERED **00-00-2011 to 00-00-2011**

4. TITLE AND SUBTITLE **A Comprehensive Environmental Assessment Approach to Making Informed Decisions about Engineered Nanoparticles**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Army Engineer Research and Development Center,Environmental Laboratory,3909 Halls Ferry Road,Vicksburg,MS,39180-6199**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**30**	

Standard Form 298 (Rev. 8-98)
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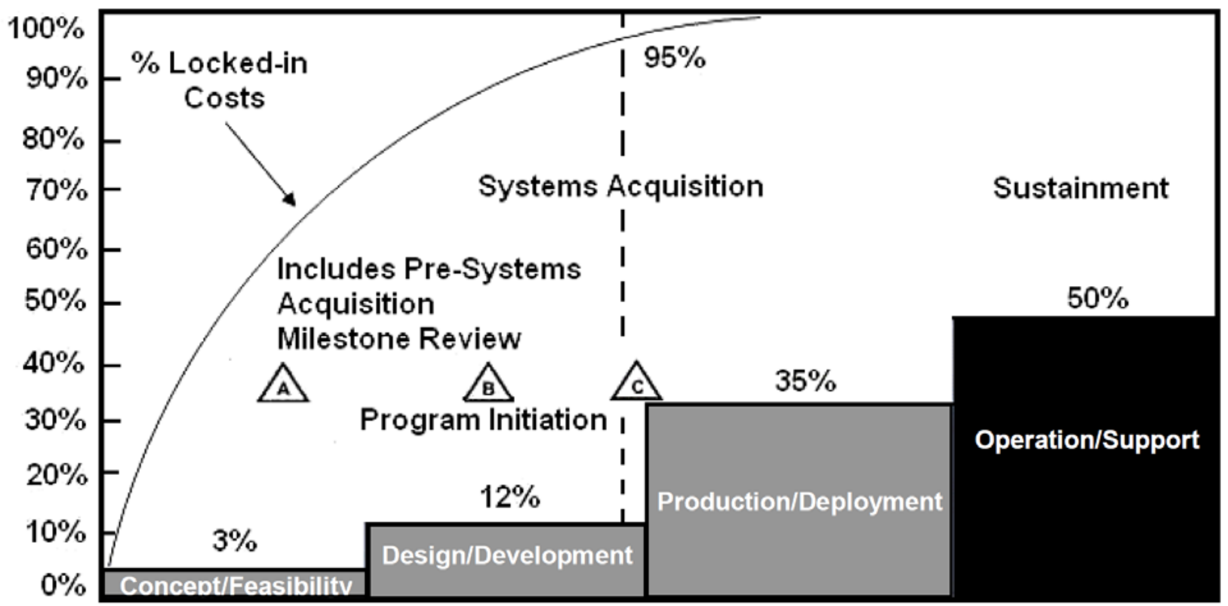
DoD Materiel Development and Costs



Phase graphics: Robert Cramwell, Sandia National Laboratories, *Ground Vehicle Reliability*, DoD Maintenance Symposium, November 13-16, 2007.

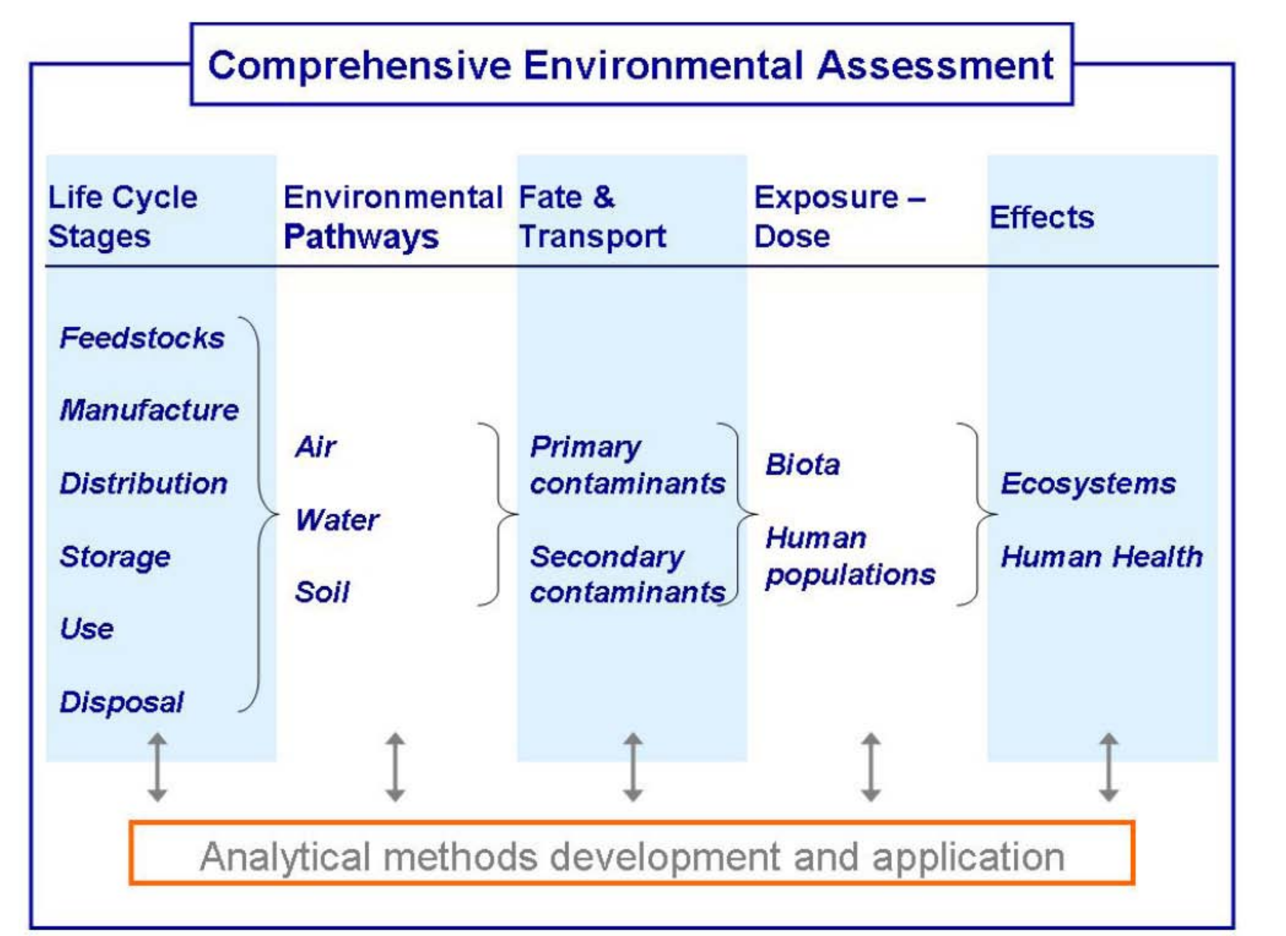
<u>Challenges</u>:

•Regulations (e.g., EU REACH)
•Limited EHS information
•Limited field data & exposure information
•Cost
•Time

- **It is estimated that <u>over 85%</u> of the costs of technology occur <u>after</u> systems acquisition**

Comprehensive Environmental Assessment (CEA)

Known Knowns

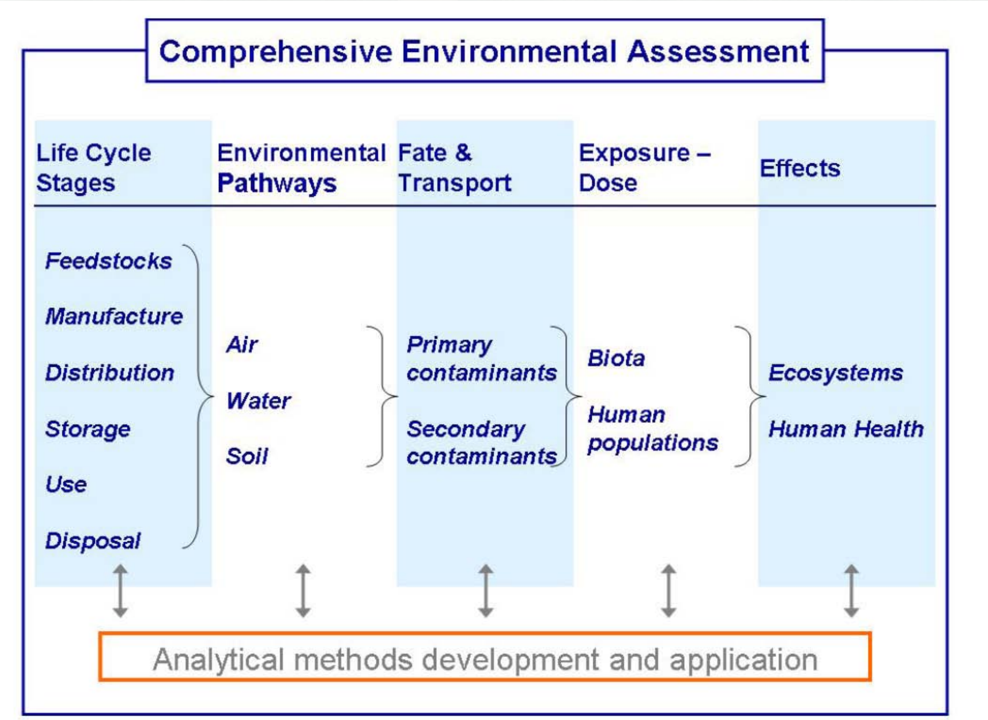


Known Unknowns

Unknown Unknowns

Adapted from Davis, 2007

CEA: Lessons Learned with fuel oxygenate MBTE



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(1) A multimedia environmental perspective built on a product life cycle framework is essential.

(2) A by-product may be more problematic than the primary substance.

(3) Human health is not the only issue of concern.

(4) Use caution in generalizing from limited empirical data.

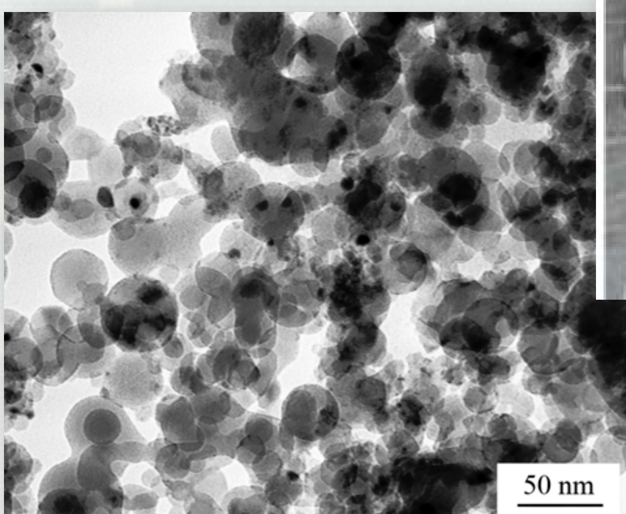
(5) The public deserves to be well-informed.

(6) Everything has trade-offs: some may be acceptable, some may not.

(7) Even with limited information, technical experts may be able to anticipate risks.

(8) An adaptive risk management strategy is critically important.

ERDC CEA Case Study: Engineered Aluminum Nanoparticles



Applying CEA approach to nanotechnology in the R&D Phase

Known Knowns

- Lack of mature industries
- Data lacking or evolving
- Characterization of materials
- Uncertainty is high
- Identify and prioritize knowledge gaps

Known Unknowns

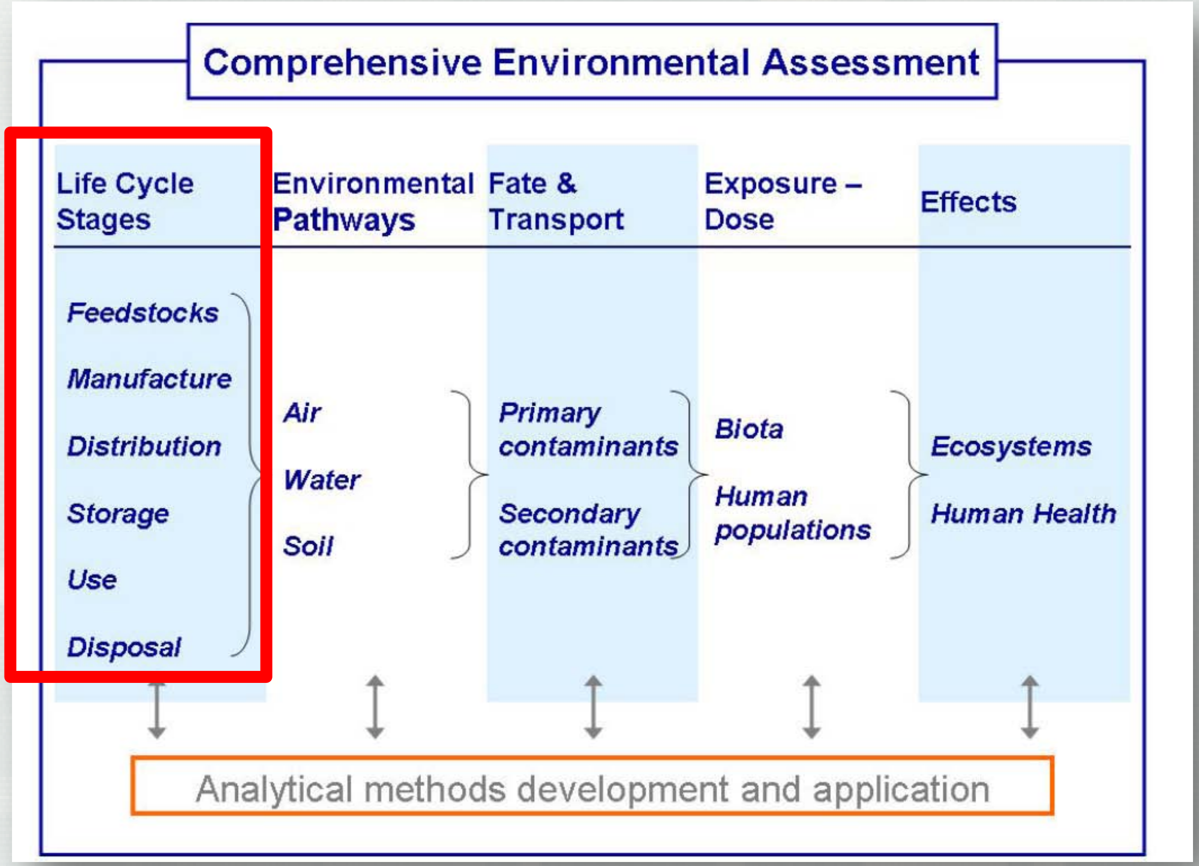
Unknown Unknowns

CEA Process

- **Identify the question(s)**
  - Sources
  - Life cycle stages, fate & transport, matrices, exposure, effects
  - Developed methods and standardized protocols
- **Obtain diverse perspectives**
  - **ODUSD** Chemical & Material Risk Management
  - **NNCO** National Nanotechnology Coordination Office
  - **ARMY-** ARDEC , Army Institute of Public Health, ERDC
  - **Navy-** NSWC-IHD
  - **Air Force-** Air Force Laboratory Human Effectiveness Directorate
- **Use collective judgment method**

Adapted from Davis, 2007

CEA: Life Cycle Stages of nano-Al



Life Cycle Stages: Feedstocks & Manufacturing

Top-Down Synthesis

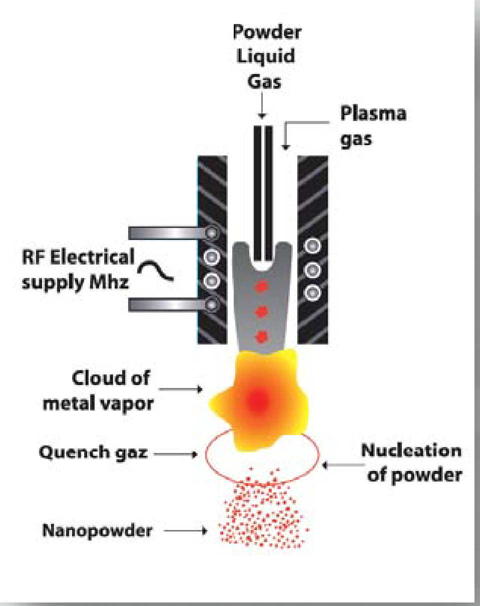
- **Milling technique (micron-sized Al particles to nanosized powder)**
- **Vaporization technique (Al rods)**

Bottom-up synthesis

- **Solution technique**

Both

- **Plasma synthesis**
- **ARDEC Picatinney Arsenal Nanotechnology Research Center: Radiofrequency (RF) Induction Plasma reactor (Tekna Plasma Systems) pilot plant**



Synthesis Challenges: (1) Particle Sizes, (2) Nanoparticle oxidation

<u>Life Cycle Stages</u> – Distribution and Storage

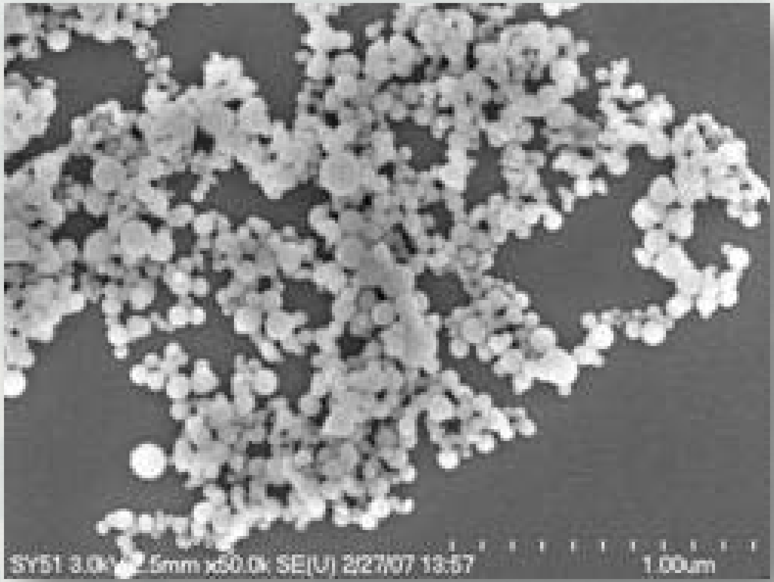
•Use of nano-aluminum still in the R&D phase

•Stored under inert atmosphere

•Aggregates are stored at the facility (still have research value),

•Current synthesis of 200g batches for rapid characterization

•Stability studies indicate no loss in surface area, however a 20% loss in reactivity due to oxygen diffusion

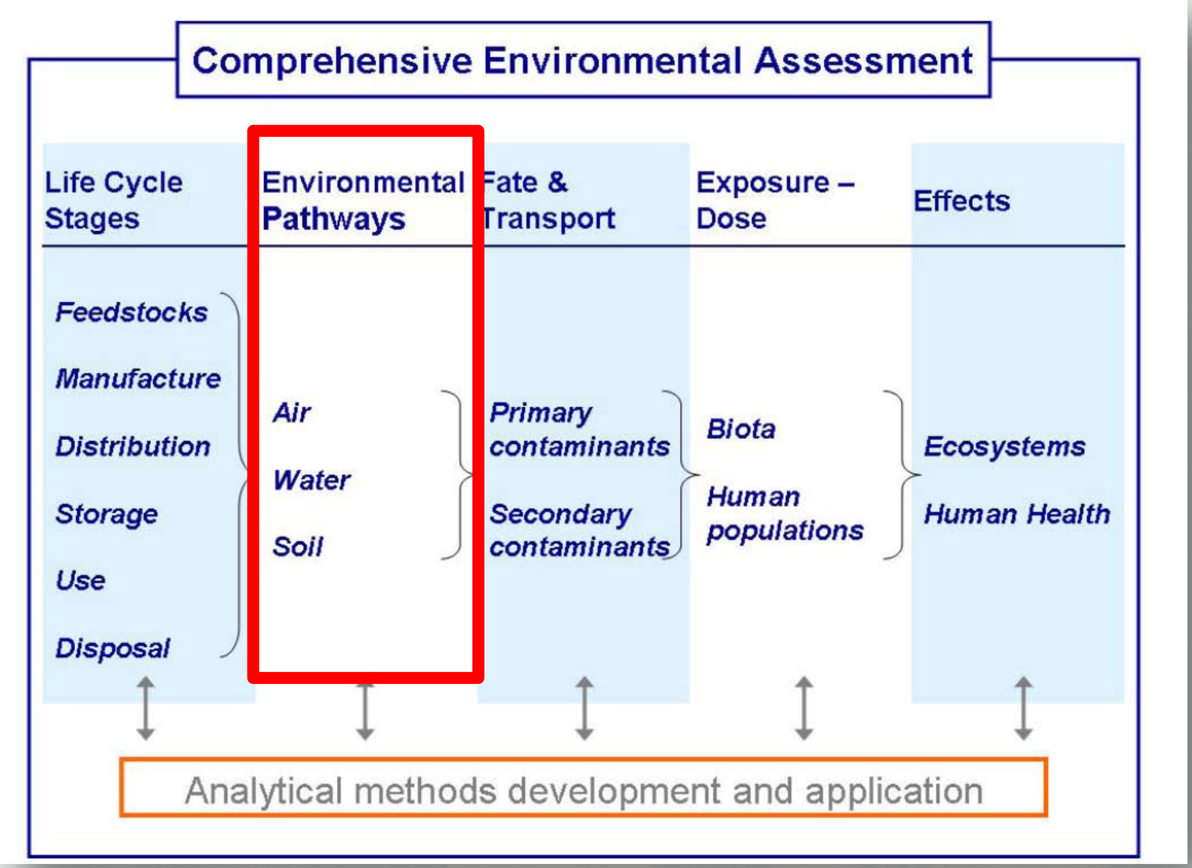


Life Cycle Stages – Use and Disposal

Potential Uses:
- Propellant
- Explosives
- Munitions primers
- Diesel fuel additive

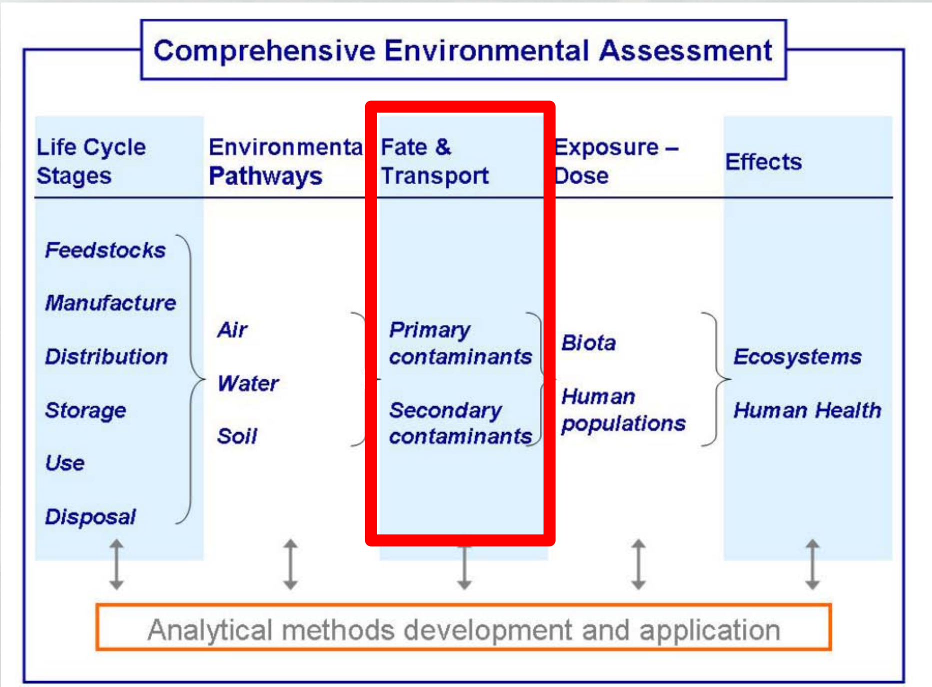
Potential Disposal Routes:
- Traditional landfills
- Wastewater streams
- Hazardous waste storage

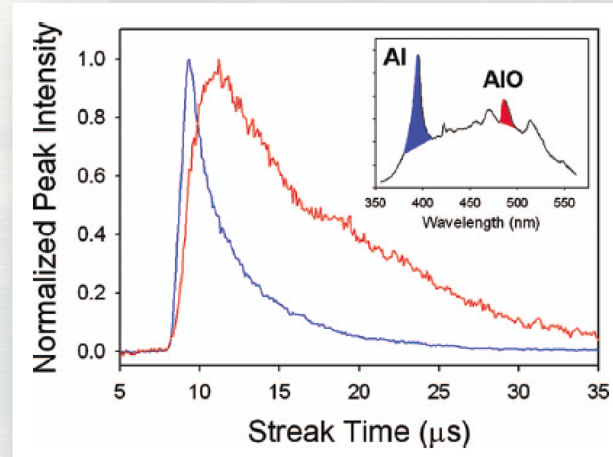
Environmental Pathways of nano-Al



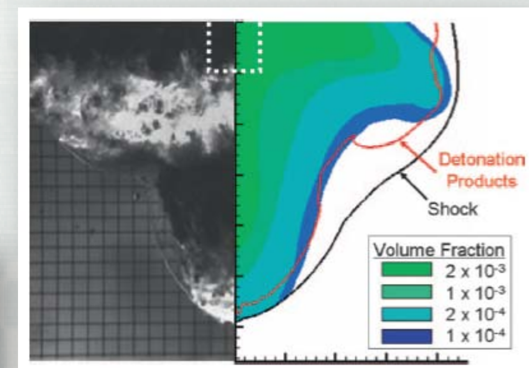
Most Likely Exposure Pathways:
Air > Soil >Water

CEA: Fate and Transport of nano-Al





Carney et al. (2006)



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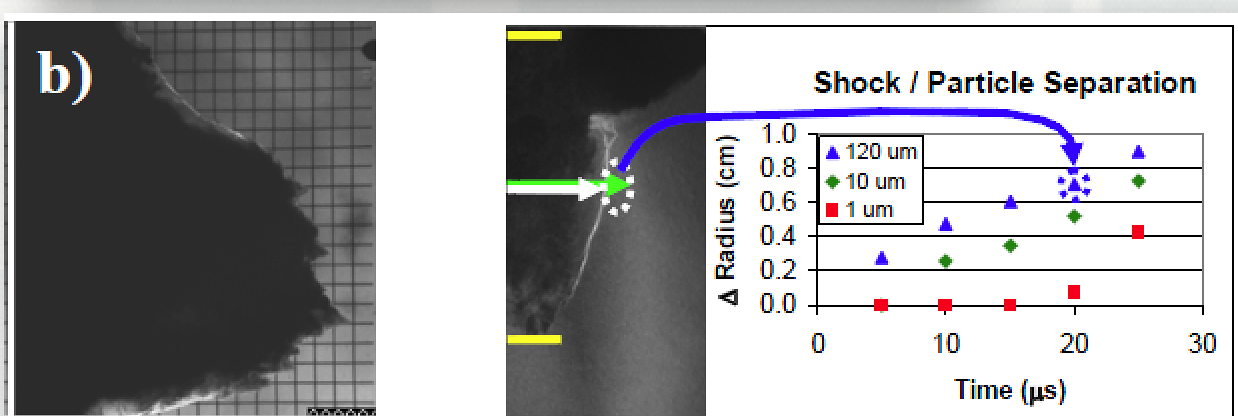
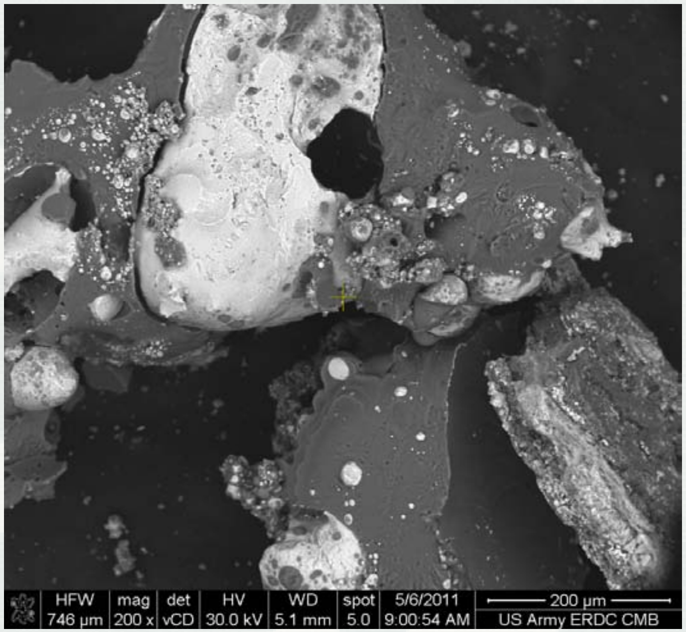
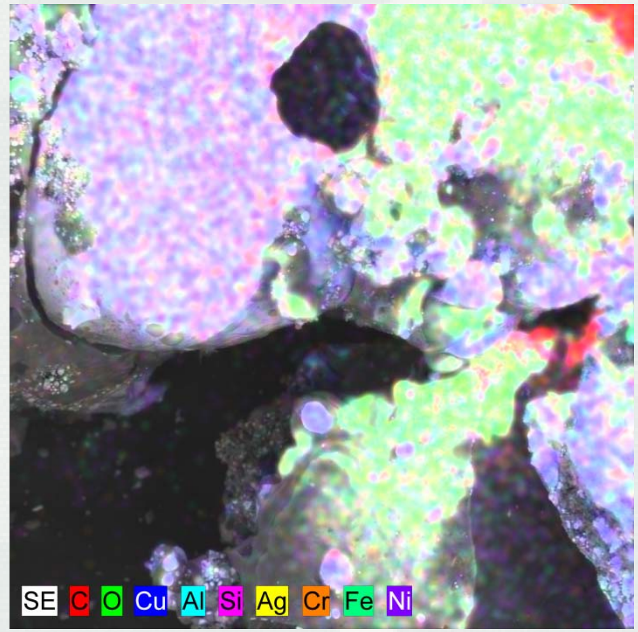
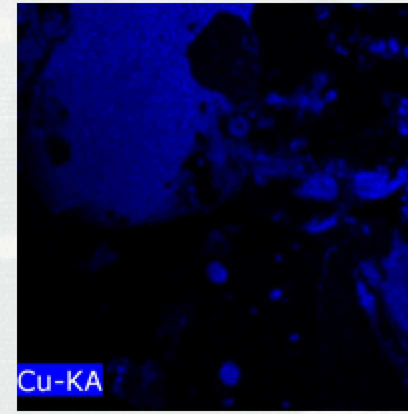


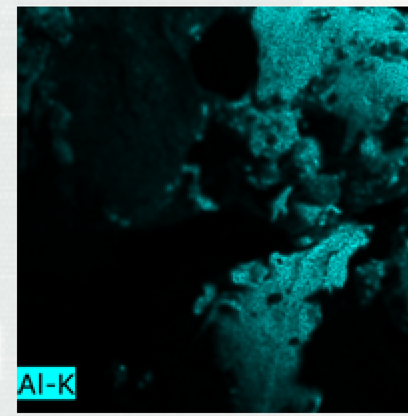
Carney et al. (2006)

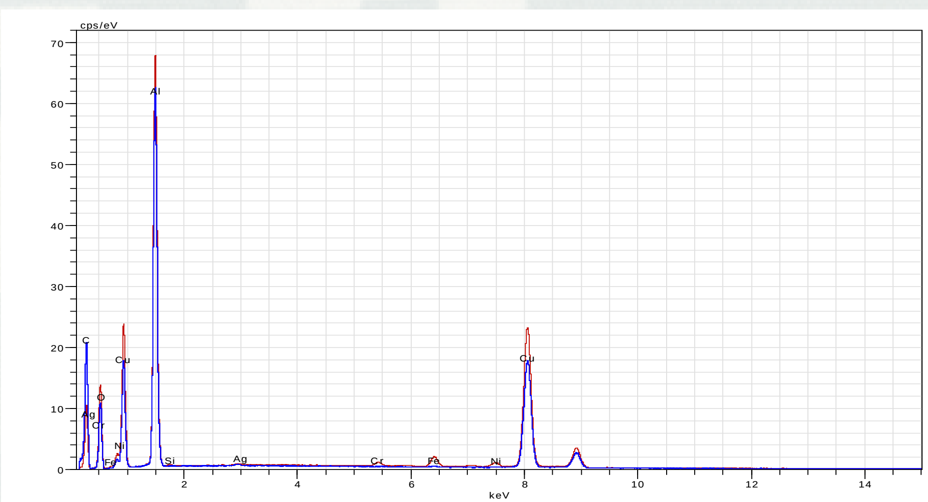
CEA: Simulated Explosion of CuO Nanorods and Al NPs





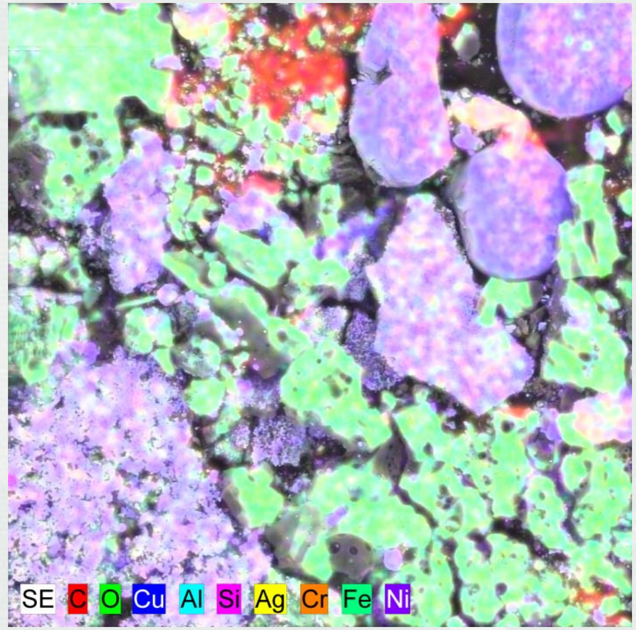


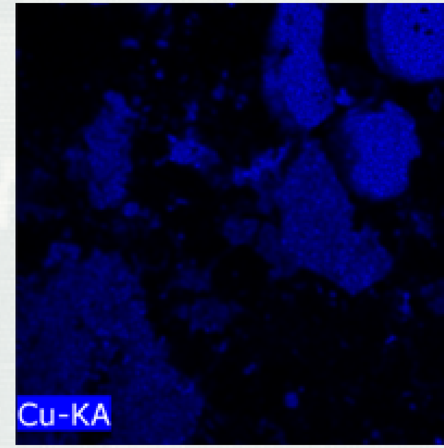


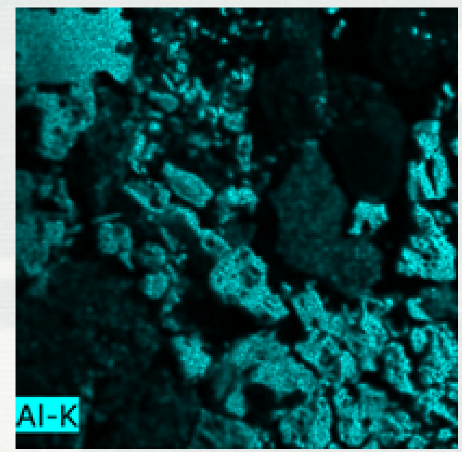


- Explosion resulted in sintered particles and nanosized metal particles
- Residue: 36.5% Al, 58% Cu

CEA: Simulated Explosion of CuO Nanorods and Al NPs







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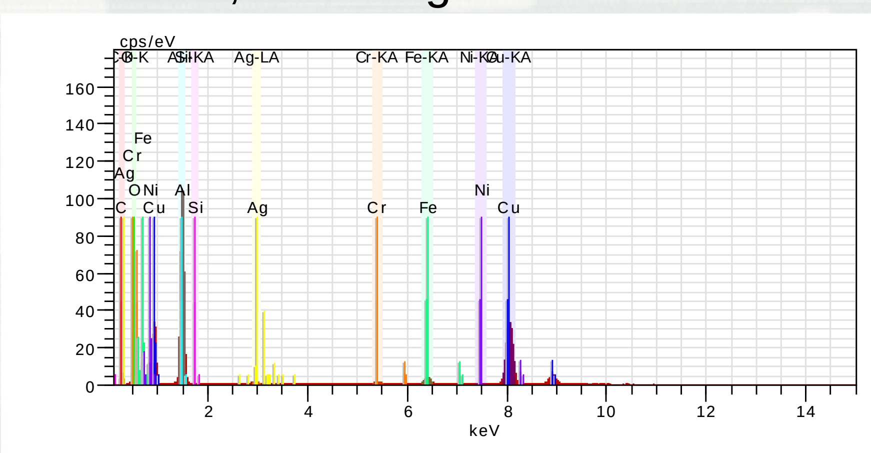


CEA: Fate and Transport of nano-Al

- Al is rapidly oxidized
  - Oxide coat stabilizes the particle and particle shape

- Particle size greatly influences oxidation potential

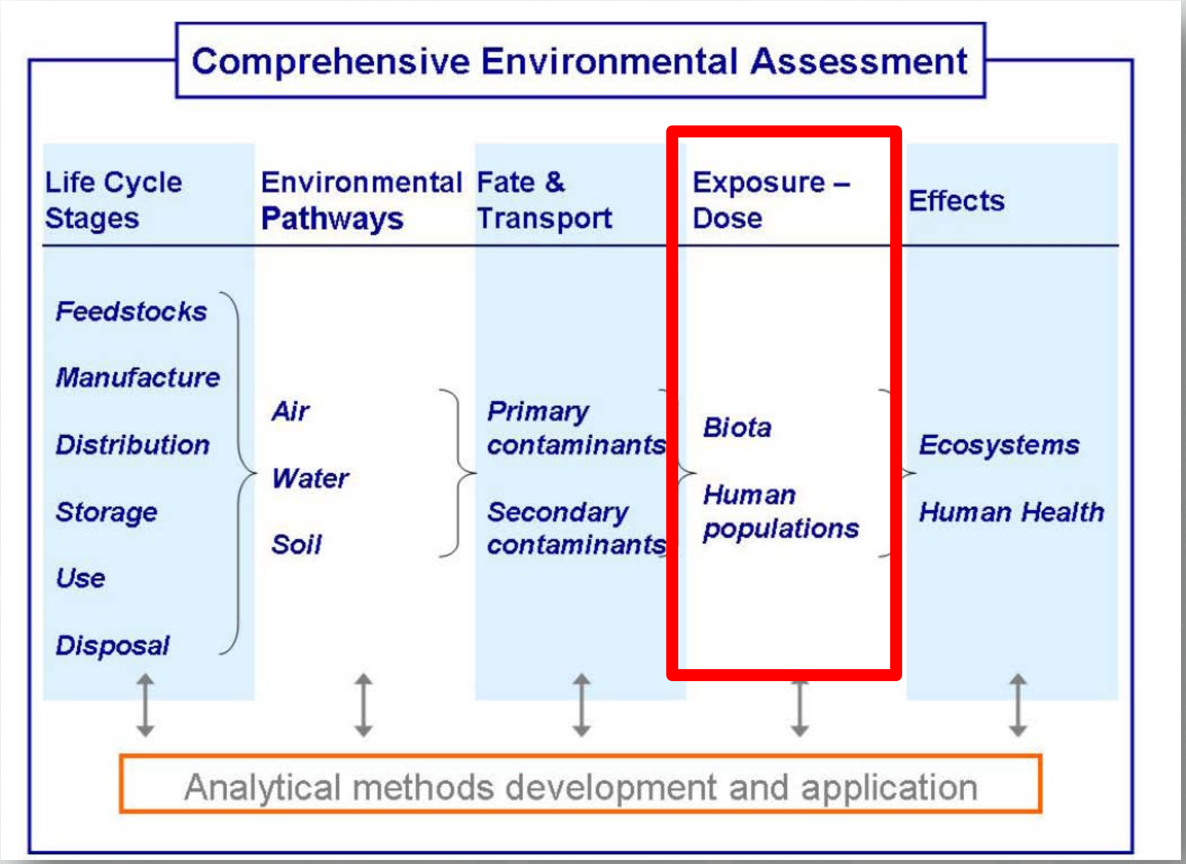
- Nano-Al/Al_2O_3 interacts with soil ,water , and strongly with humic acids

- Highly agglomerates ➡ affects mobility in soil

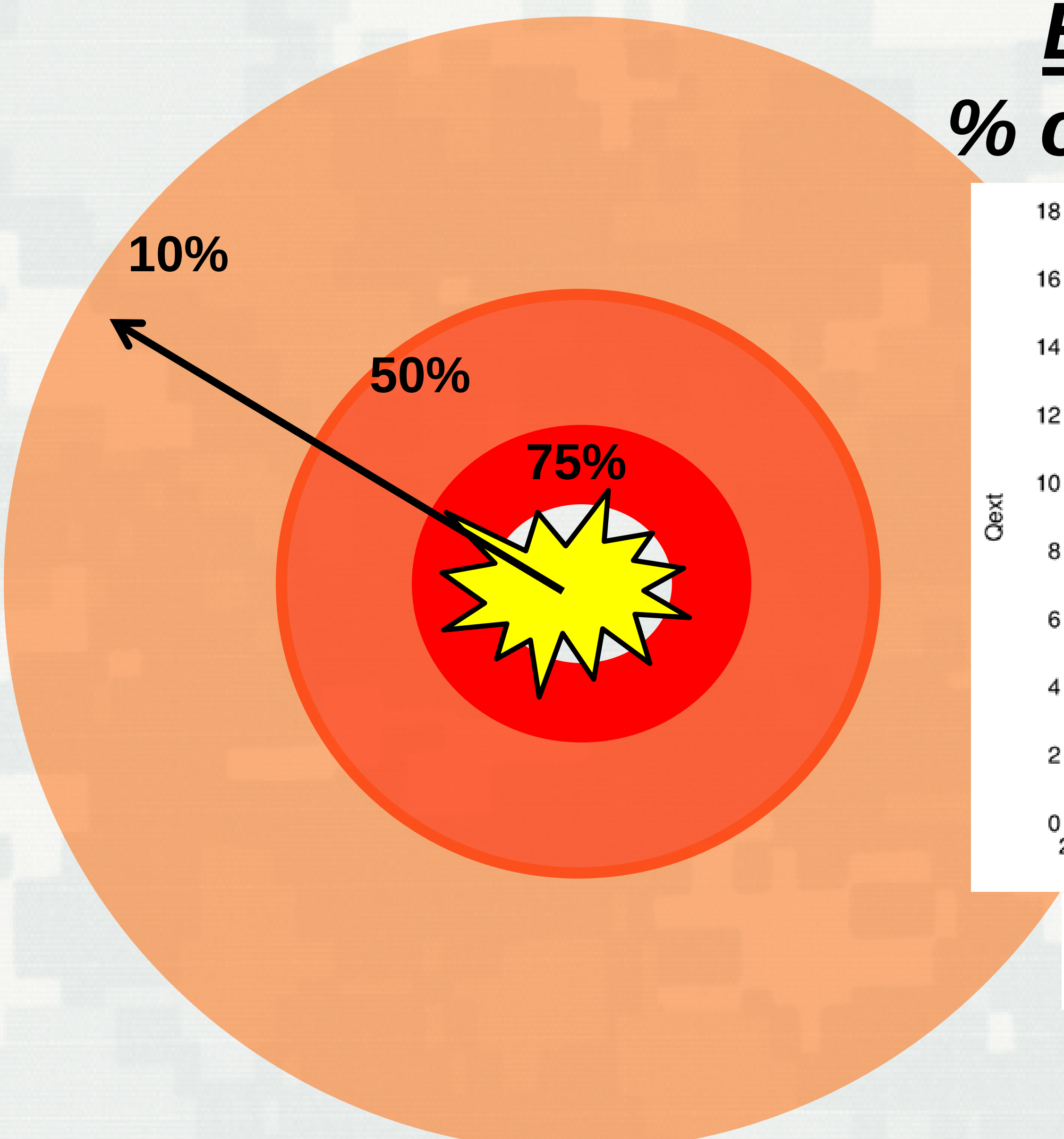
- Surface charge changes with leachate ➡ alters mobility

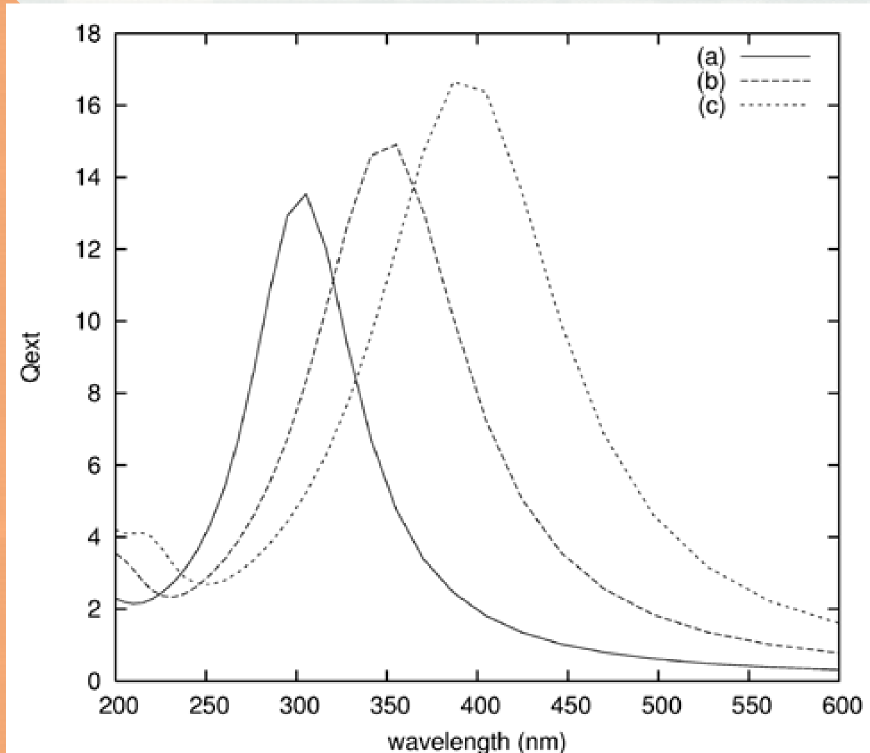
- Micron-sized Al_2O_3 has greater sorption than nano-Al_2O_3

Exposure-Dose of nano-Al



Exposure-Dose
% content of nano-Al





Plot of extinction values for Al triangular prisms (Faber et al. 2008)

Exposure-Dose of nano-Al

Most likely routes of nano-Al/Al_2O_3 exposure:

Inhalation > Internal (mucociliary escalator) > Dermal > Internal (oral)

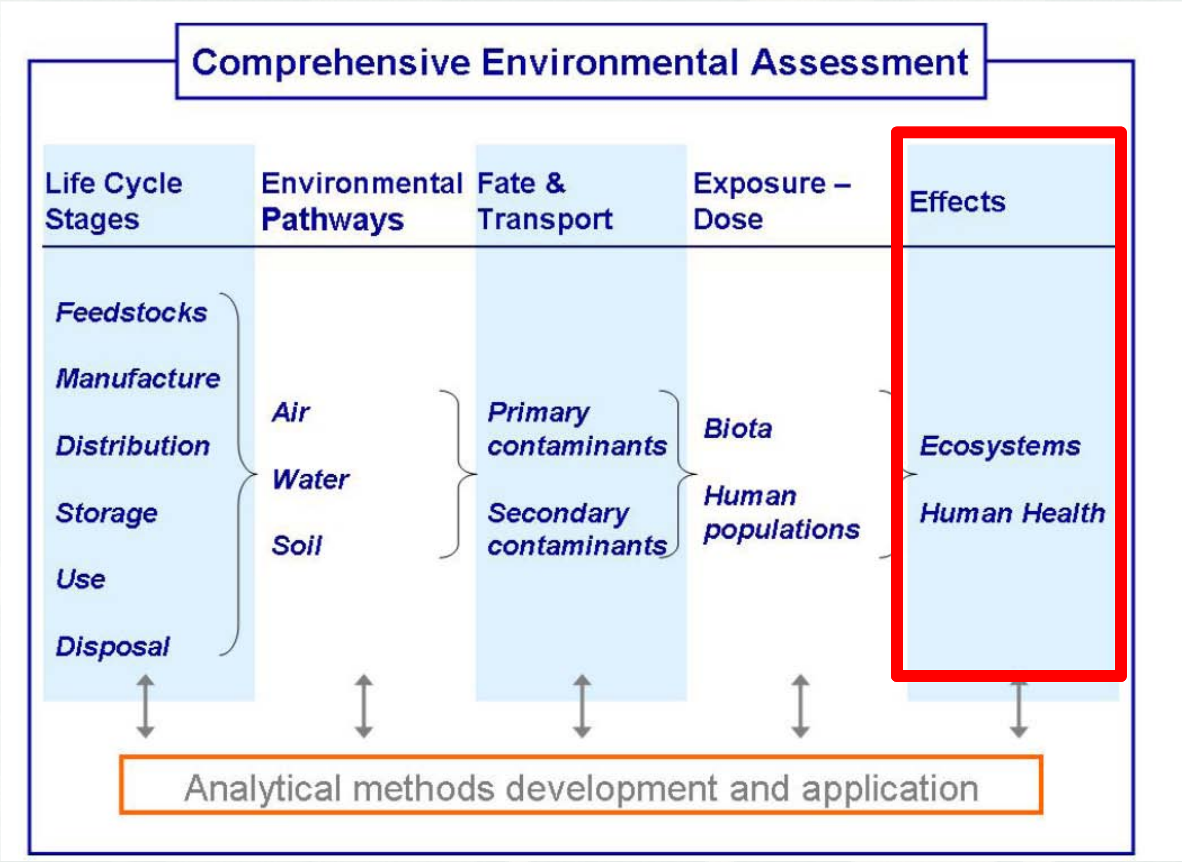
ARDEC-NIOSH collaborative framework *"Nano-powder Synthesis & Associated Safety Precautions at ARDEC"*

TWA and other occupational exposure values?

R&D laboratory evaluations of occupational exposures?

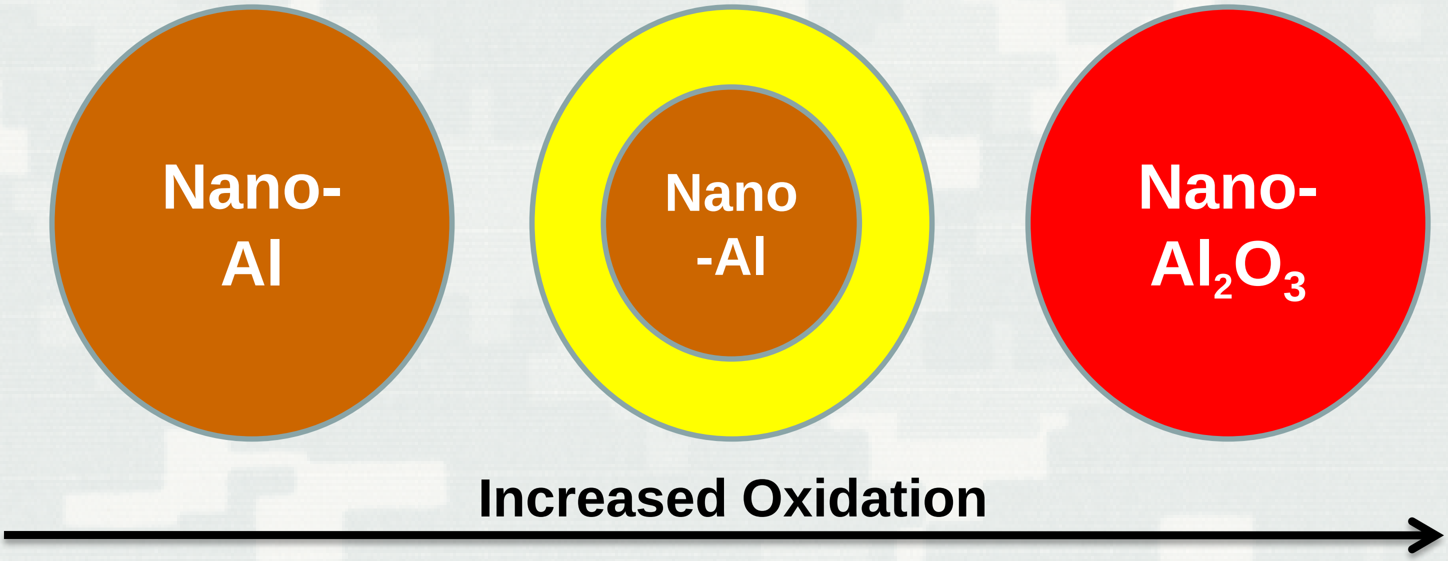
Evaluate exposures in the field and firing ranges

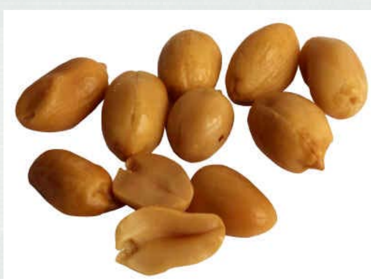
***Effects* of nano-Al**

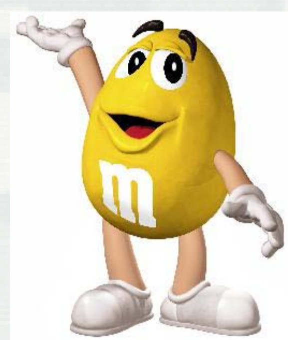


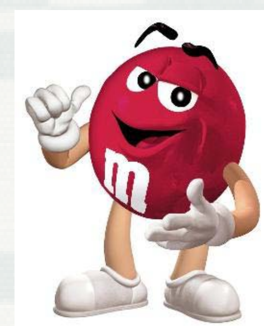
Problems with <u>Effects</u> of nano-Al

- **Nano-Al/Al_2O_3 is highly agglomerated**
- **Is aged nano-Al the same as nano-Al_2O_3?**







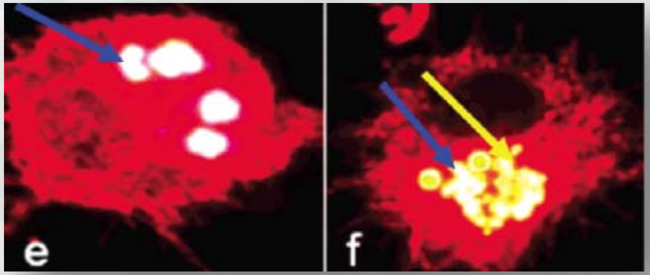


Effects of nano-Al: Ecosystems

Most Likely Exposure Pathways:
Air > Soil >Water

- **Aquatic**
  - **Less toxic to daphnids and algae than other NPs**
  - **More toxic to juvenile zebrafish than adults**
  - **Causes atherothrombotic events in zebrafish**
  - **Produces differential effects on benthic organisms**
- **Terrestrial**
  - **Mildly toxic to bacteria**
  - **Mildly phytotoxic (root growth inhibition) due to ROS**
  - **Soil nematodes and earthworm reproduction negatively affected, yet actively avoid nano-Al spiked soils**

Effects of nano-Al: Human Health



1.Inhalation

•Nano-Al, not Al_2O_3, negatively affects alveolar macrophages function

•Suppressed macrophage ability to fight respiratory pathogen MRSA

•No *in vivo* studies yet

2.Dermal

•Dermal contact may increase proinflammation, dermatitis

•Accumulation likely in epidermis, but not dermis & no bioaccumulation

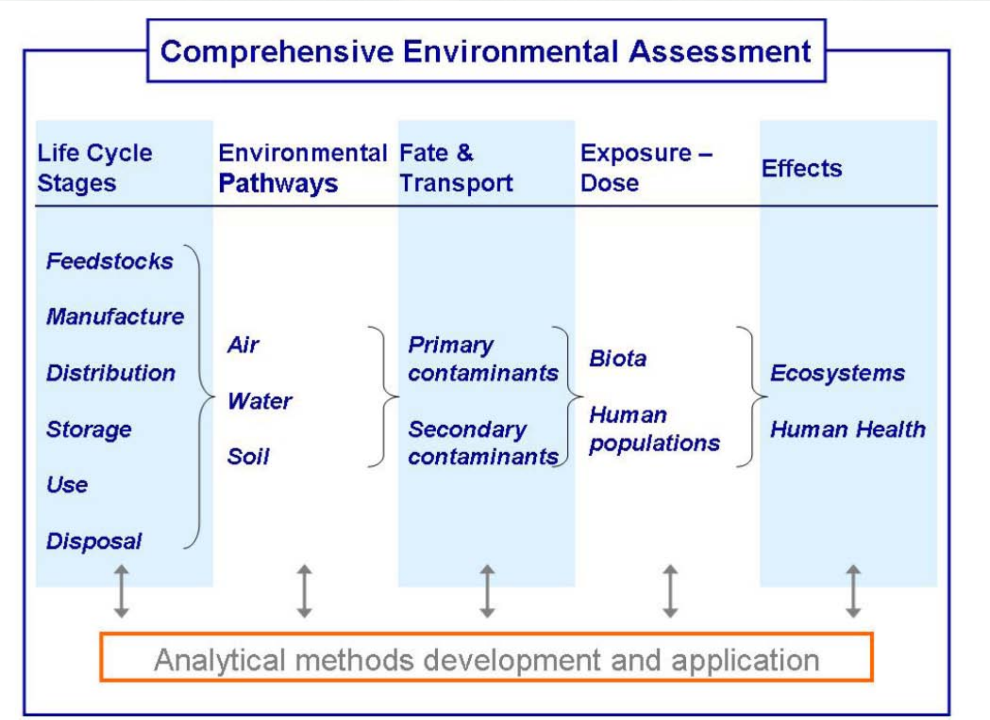
3.Internal

• Cell damage in several *in vitro* studies using internal organ cultures

•Neurotoxicity (blood brain barrier disruption) and

• Genotoxicity *in vivo* and *in vitro*, secondary to ROS (?)

CEA: Lessons Learned with fuel oxygenate MBTE



Adapted from Davis, 2007

(1) A multimedia environmental perspective built on a product life cycle framework is essential.
(2) A by-product may be more problematic than the primary substance.
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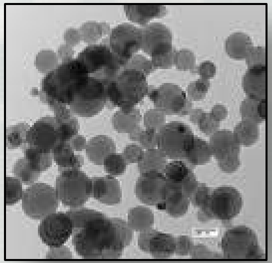
(4) Use caution in generalizing from limited empirical data.
(5) The public deserves to be well-informed.
(6) Everything has trade-offs: some may be acceptable, some may not.
(7) Even with limited information, technical experts may be able to anticipate risks.
(8) An adaptive risk management strategy is critically important.

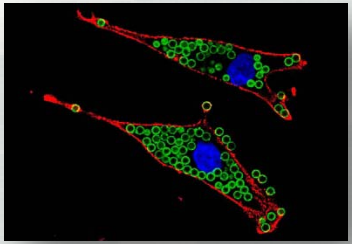
Preliminary Conclusions

- Potential sources and releases of nano-Al to the environment that will likely occur through air, water, or soil exposures through the production, use, and disposal of nano-Al propellants, igniters, and additives.

- However, these preliminary findings are the result of an assessment from the R&D community.

- Data collection is still required to gain a better understanding of the future deployment and handling of nano-Al as a military technology.





Data Gaps/ Moving Forward

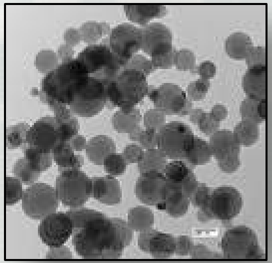
•***Life Cycle*: ** Further collaboration required within the R&D community such ARDEC, NSWC-IHD, and AFRL to discuss life cycle phases.

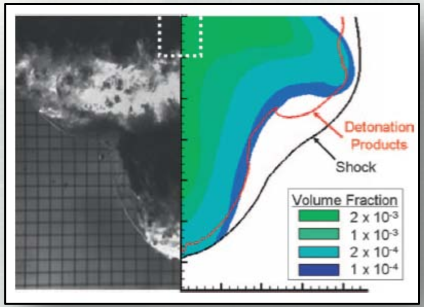
•***Environmental Pathways*: ** (1) combustion analyses, (2) atmospheric deposition field studies, (2) atmospheric modeling of firing ranges

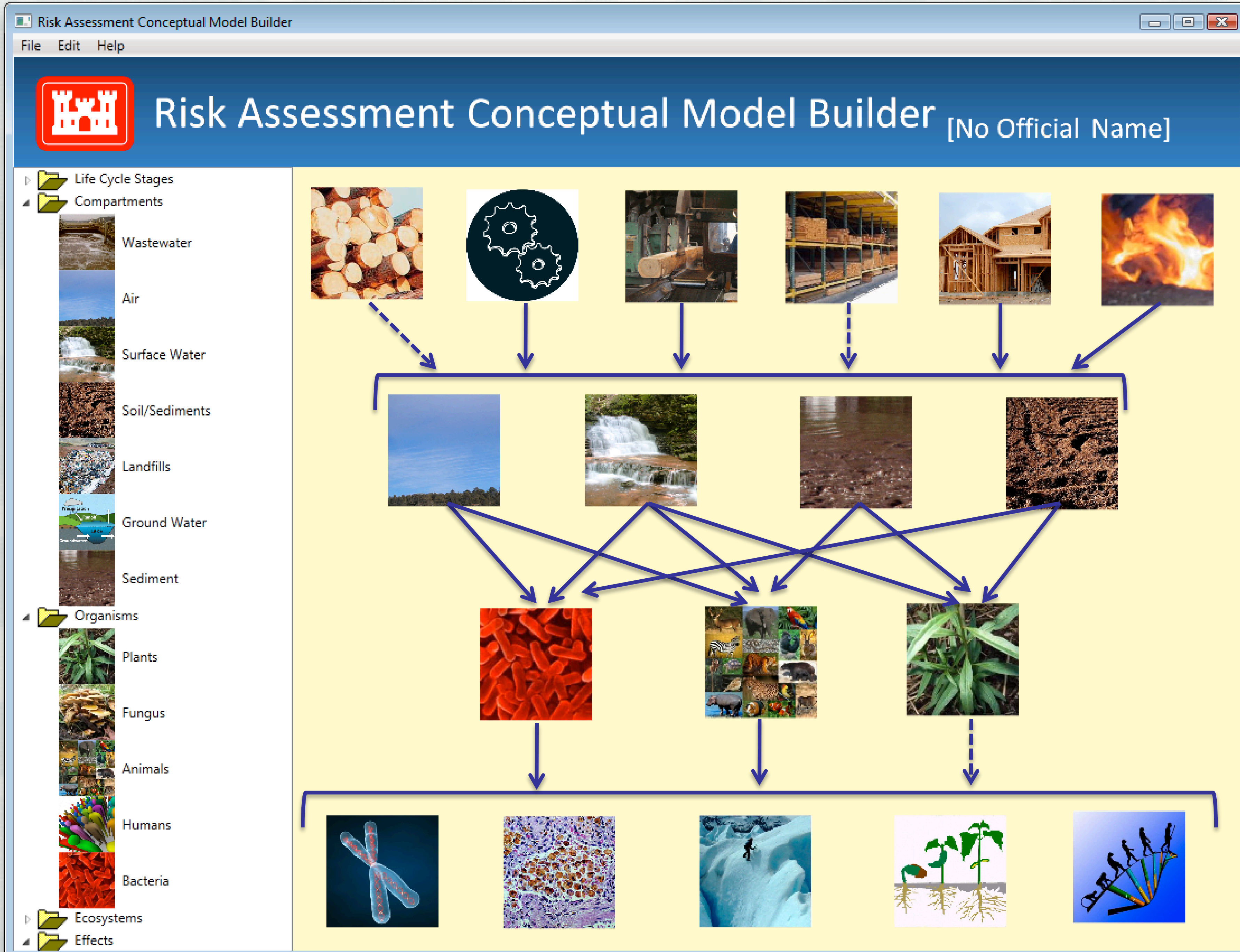
•***Exposure***: *In vivo* exposure to biota and humans is perhaps the biggest area of uncertainty in this entire nano-Al CEA.

•***Environmental Fate***: (1) environmental characteristics (e.g., temperature, weather) effects on nano-Al aging, (2) field studies with military materiel (munitions, propellants, etc.)

•***Effects***: Data needs to reflect of actual particle sizes, i.e. nanoparticle agglomerates vs. monodispersed nanoparticles.



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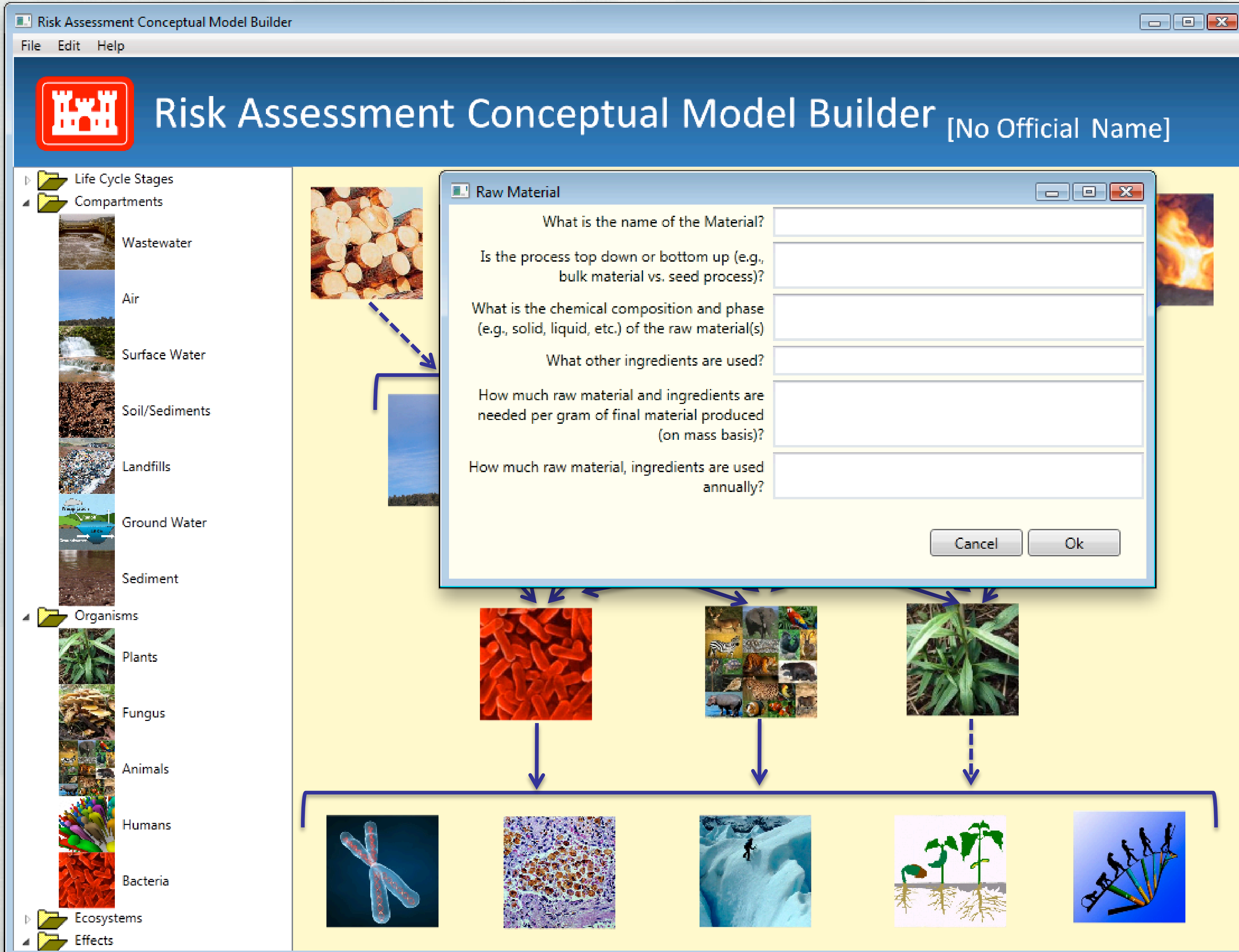
Life Cycle Stages
Compartments
Wastewater
Air
Surface Water
Soil/Sediments
Landfills
Ground Water
Sediment
Organisms
Plants
Fungus
Animals
Humans
Bacteria
Ecosystems
Effects



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Sediment
Organisms
Plants
Fungus
Animals
Humans
Bacteria
Ecosystems
Effects
Raw Material
What is the name of the Material?
Is the process top down or bottom up (e.g., bulk material vs. seed process)?
What is the chemical composition and phase (e.g., solid, liquid, etc.) of the raw material(s)
What other ingredients are used?
How much raw material and ingredients are needed per gram of final material produced (on mass basis)?
How much raw material, ingredients are used annually?
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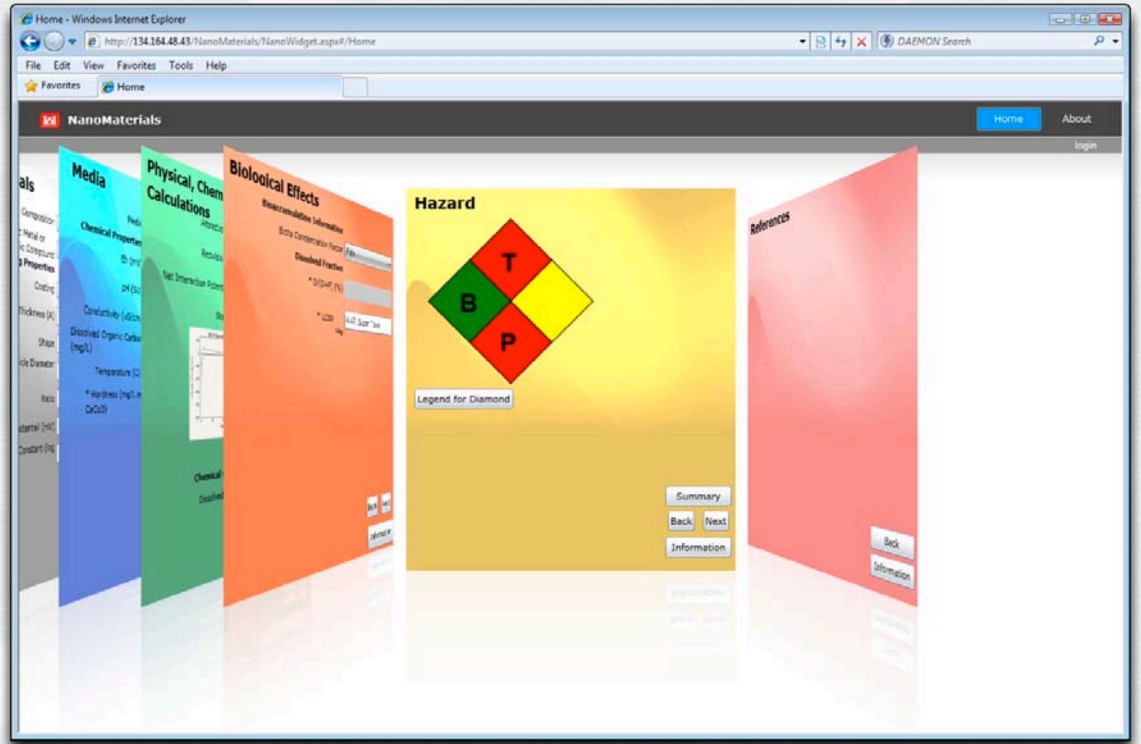
Ok

NanoExPERT



Categories:

- **Materials**
- **Media**
- **Physical, Chemical, Model, and Caculations**
- **Biological Effects**
- **Hazard**

ERDC Environmental Nanotechnology Team

http://el.erdc.usace.army.mil/nano/index.html

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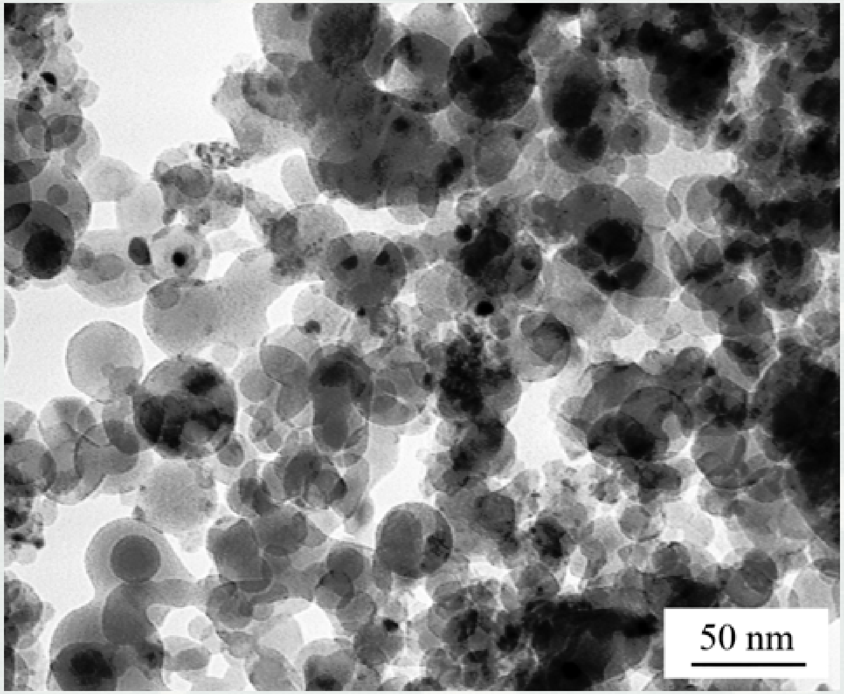
<u>Material Science</u>: Chuck Weiss
<u>Biology</u>: Al Kennedy, David Johnson, Jacob Stanley, Cynthia Banks
<u>Computer Science</u>: Amy Bednar



•Critical review and advising from Dr. Mike Davis, Senior Science Advisor, U.S. EPA and Dr. Thomas Seager, Professor, University of Arizona
•This research effort was funded by an ERDC Center Directed Research Project, "Comprehensive environmental assessment for nano-enabled defense and deal use capacities," Dr. Jeff Holland, ERDC Director.
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